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Direct Synthesis of Poly(lithium organoborate)s and Their Ion Conductive Properties

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Synthesis of inorganic polymers[1] has been a great deal of synthetic challenge for the past several decades. Even though relatively limited variation and utility of inorganic chemistry have prevented the facile synthesis of a variety of stable inorganic polymers composed of exotic bondings, such materials reported to date were found to possess unique characteristics such as low-temperature flexibility, high thermal or oxidative stability, nonflammability and unique electrical and optical properties.

Recently, as a new class of inorganic materials, organoboron compounds are attracting growing interest these days in view of application for light emitting materials, NLO materials, anion sensor, ion conductive materials, etc.[2–4] The pioneering work by Chujo et al. demonstrated that some organoboron polymers[3] are sufficiently stable to serve as a novel type of functional materials. We have extended such method for the preparation of well-defined organoboron polymer electrolytes[4] which showed selective ion transporting property via anion trapping effect of the boron atom.

In the present work, as a new class of organoboron polymer, poly(lithium organoborate)s were prepared by dehydrocoupling polymerization between lithium mesitylhydroborate and oligo(ethylene oxide) and subsequent treatment with alcohol (Scheme 1b). The obtained polymers were evaluated with regard to ion conductive characteristics by means of ac impedance method.

As a single ion conductive inorganic polymer electrolyte, lithium aluminate type polymers have been investigated by several research groups.[5] Because of the relatively high dissociation degree of lithium aluminate type ate-complex, these polymers exhibits moderate ionic conductivity. However, limited variation of aluminum chemistry prevents further development of these materials. Therefore, incorporation of another ate-complex such as lithium borate is an interesting approach for the preparation of novel single ion conductive polymers showing improved ion conductive property. We have recently reported the preparation of lithium borate polymer electrolytes by polymer reaction of well-defined organoboron polymer with organolithium reagents.[4b] On the other hand, Angell et al.[6] reported PEO derivatives having lithium orthoborate structure at the chain end. Sodium borate type materials derived from sodium hydroborate was also reported by Fujinami et al.[5b] Because of the diversity of organoboron chemistry and reasonable stability of aromatic organoboron unit, borate type polymer electrolytes should have a considerable potential as a new class of single ionic conductor. However, in our previous study,[4b] borate type polymer electrolytes prepared by polymer reaction using organolithium reagents did not show very high conductivity (Scheme 1a). When *n*-butyllithium was used, decomposition of the polymer was indicated from ^{1}H and ^{11}B NMR spectra. On the other hand, a polymer reaction using phenyllithium suffered low conversion due to relatively low reactivity of phenyllithium with the mesitylboron unit. Furthermore, after the polymer reaction with phenyllithium, incorporation of phenyl group as side chain raised glass transition temperature of the polymer by approximately 20 °C, which resulted in lower ionic conductivity.

In the present study, to avoid these drawbacks of previous system, direct synthesis of borate type polymer electrolyte using lithium mesitylhydroborate was ex-

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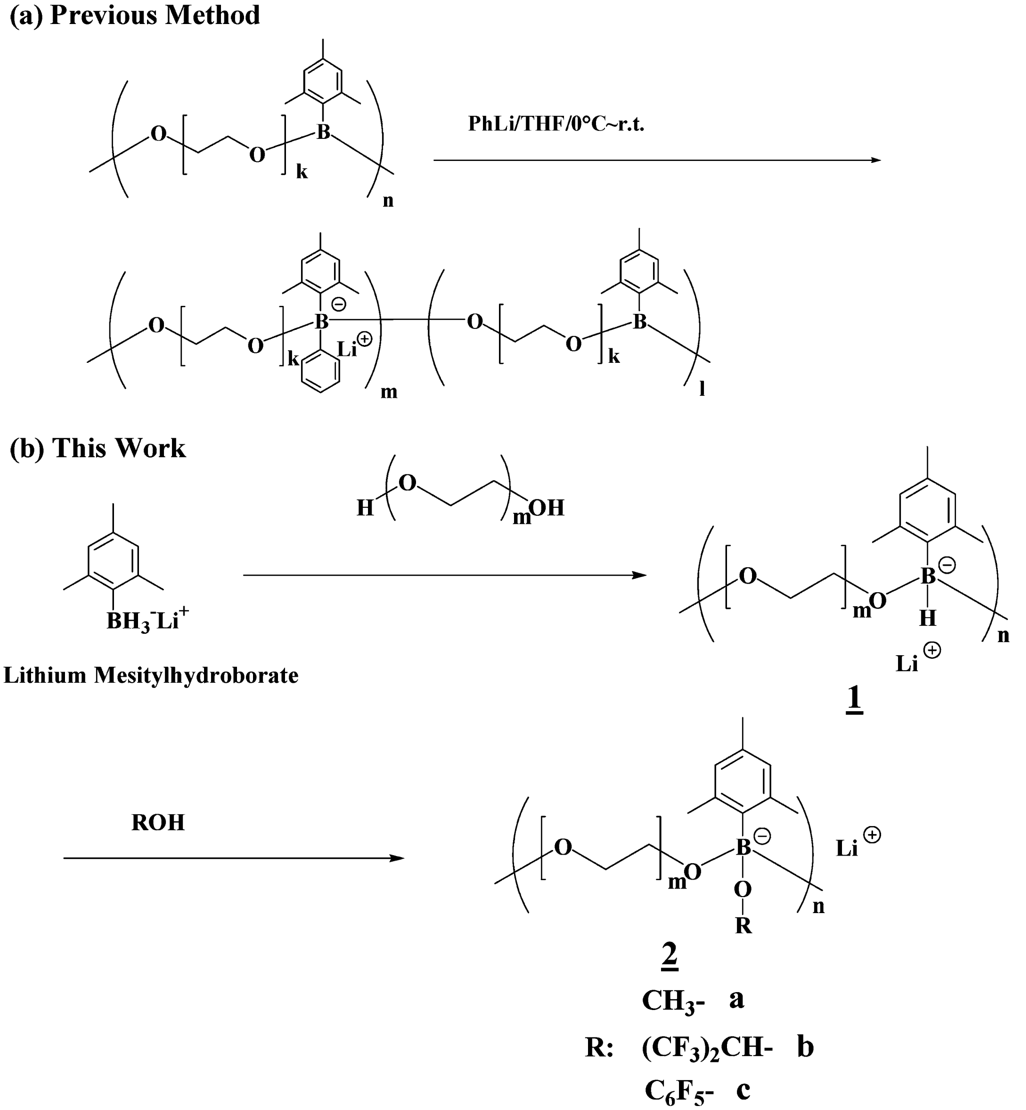
Scheme 1



amined to give the corresponding polymers bearing borate structure in every repeating unit. This synthetic method is expected to lead to improved ionic conductivity of the resulting polymers because of greater number of mobile carrier ions and the absence of aryl groups originating from aryllithium reagent.

Lithium mesitylhydroborate [7] was prepared according to the reported method by reaction of mesitylmagnesium bromide with trimethoxyborane and subsequent reduction with $LiAlH_4$. The preparation of borate polymer electrolytes was examined by dehydrocoupling polymerization[3c] of oligo(ethylene oxide) with lithium mesitylhydroborate. The polymerization was carried out under nitrogen atmosphere by adding a THF solution of a slightly excess lithium mesitylhydroborate to oligo(ethylene oxide) in THF as depicted in Scheme 1b. After stirring the reaction mixture for 6 h, the resulting polymers were purified by reprecipitating them into *n*-hexane and washing with ether, to give white gum in 61−76% yield. After the treatment with alcohols, the polymers **2a**−**2c** were obtained as transparent soft solid soluble in common organic solvents such as methanol, THF, and chloroform.

The structures of the polymers were confirmed by ^1H and ^{11}B NMR spectra (in $CDCl_3$). In the ^1H NMR spectra of polymer **2b**, introduction of the mesityl group was confirmed from the peaks due to mesityl group at 2.14 and 6.67 ppm (Figure 1a). In the ^{11}B NMR spectrum of polymer **2b**, the main peak was observed at 22.7 ppm (Figure 1b).

Since poly(lithium organoborate)s are relatively moisture sensitive, it is necessary to be treated under dry atmosphere. However, when stored under inert atmosphere, poly(lithium organoborate)s showed identical ^1H and ^{11}B NMR spectra even after keeping them for several weeks.

The molecular weight of poly(lithium mesitylhydroborate) prepared from PEO400 was estimated by GPC measurement (polystyrene standard) to be 2800 at the peak top. The estimated molecular weight was relatively low, however, taking more rigid nature of polystyrene standards than PEO derivatives into account, actual M_w of the polymer should be greater.

Before treatment with alcohols, poly(lithium mesitylhydroborate)s prepared from oligo(ethylene glycol) with various chain length showed ionic conductivity of 6.23×10^{-5}–2.07×10^{-7} S/cm at 323 K. When PEO400 was employed, the maximum ionic conductivity of 6.23×10^{-5} S/cm was observed. Therefore, poly(lithium mesitylhydroborate) bearing PEO400 unit ($m = 8.7$) was then subjected to polymer reaction with various alcohols.

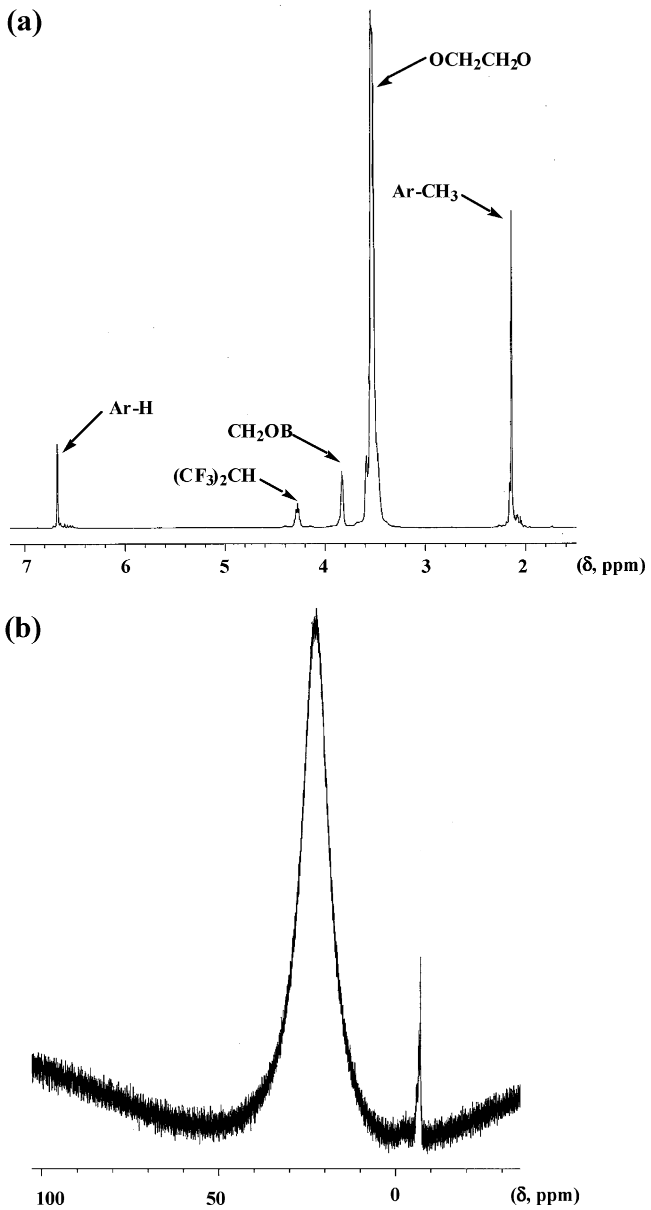


Figure 1. ^{1}H (a) and ^{11}B NMR (b) spectra for polymer **2b** in $CDCl_3$.

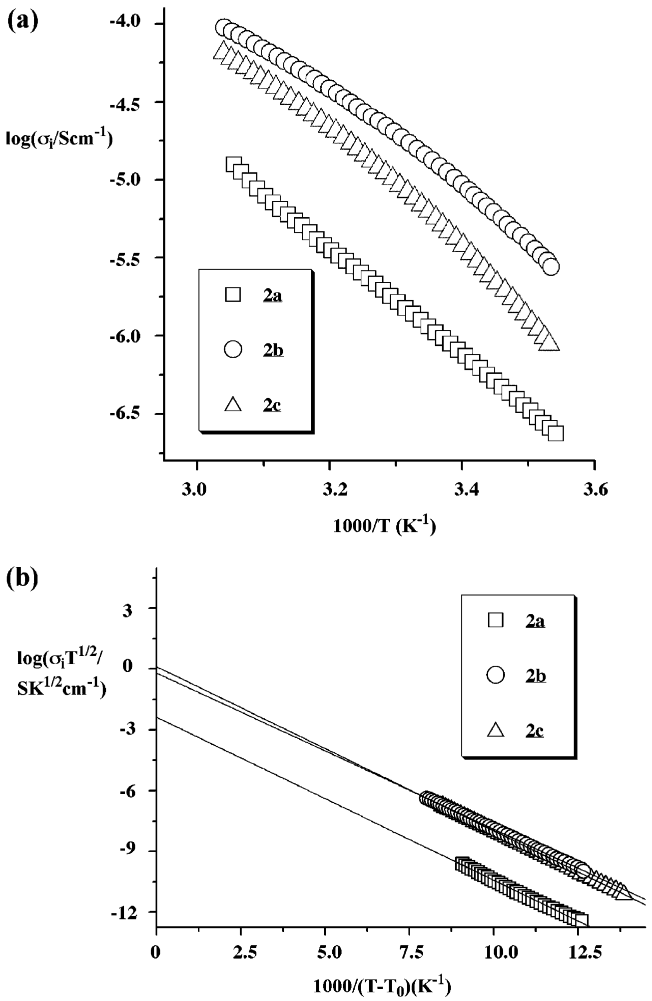


Figure 2. (a) Temperature dependence of ionic conductivity and (b) VFT plots for poly(lithium organoborate)s.

Table 1. Ionic Conductivity, T_g, and VFT Parameters for Polymers *2a*–*2c*

polymer	σ_i (S cm^{-1}) at 303 K	σ_i (S cm^{-1}) at 323 K	A (S cm^{-1} K^{-1})	B (K)	T_g (K)	T_0 (K)
2a	1.76×10^{-6}	8.77×10^{-6}	0.31	731	221	203
2b	2.04×10^{-5}	7.44×10^{-5}	0.83	751	226	204
2c	1.02×10^{-5}	4.52×10^{-5}	1.13	818	234	211

From the differential scanning calorimetry (DSC) measurement for lithium borate polymers after treatment with alcohols, glass transition temperature was in the range of 221−234K. Although T_g was raised after the polymer reaction with alcohols [poly(lithium mesitylhydroborate); T_g 204 K], a relatively low T_g was maintained, indicating flexible nature of hydroborate type polymers appropriate as ion transporting media.

Figure 2a shows temperature dependence of the ionic conductivity for polymers **2a**−**2c** evaluated by ac impedance method. Arrhenius plots showed constant rise of conductivity with increasing temperature similarly to ordinary PEO derivatives. The observed moderate conductivity indicates that introduction of mesitylborate unit does not appear to disturb the segmental motion of the polymer chain.

The ionic conductivity of **2a** was lower (8.77×10^{-6} S/cm at 323 K) than that was before the treatment with methanol (6.23×10^{-5} S/cm at 323 K). However, this value was still greater than that for previously reported borate type polymers prepared via polymer reaction with phenyllithium (9.45×10^{-7} S/cm at 323 K). When poly(lithium mesitylhydroborate) was treated with fluorinated alcohols such as hexafluoro-2-propanol and pentafluorophenol, the obtained polymers **2b** and **2c** exhibited further improved ionic conductivity compared with the case of methanol (**2a**), possibly due to increase of dissociation degree of lithium borate unit in the presence of electron withdrawing group. The highest ionic conductivity of 7.44×10^{-5} S/cm at 323 K was observed for polymer **2b**. The polymer having pentafluorophenoxy substituent (**2c**) showed relatively larger temperature dependence of ionic conductivity probably due to stacking of aromatic rings.

The Vogel−Fulcher−Tamman (VFT) equation[8] was applied to each system (Figure 2b, Table 1). Every system obeyed a linear fitting, showing that ions were transported along with the segmental motion of polymer chain similar to ordinary PEO derivatives. The VFT parameters corresponding to activation energy and carrier ion number are listed in Table 1. The relatively greater value of A for polymers **2b** and **2c** suggests greater number of carrier ions in these systems, which should be responsible for observed higher ionic conductivity than was observed for **2a**.

In summary, a well-defined solid polymer electrolyte bearing an lithium organoborate repeating unit was directly prepared using lithium mesitylhydroborate as a monomer. After treatment with various alcohols, the obtained poly(lithium organoborate)s showed improved ionic conductivity compared with the case where organolithium reagents were employed, possibly due to increased content of lithium borate unit and absence of aryl group originating from aryllithium reagent.

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(8) Generally, the ionic conductivity of solid electrolyte obeys Vogel−Fulcher−Tamman (VFT) equation $\sigma = AT^{-1/2}\exp[-B/(T - T_o)]$, where empirical constants A and B reflect the amount of carrier ions and activation energy for ion conduction. T and T_0 correspond to temperature and ideal T_g, respectively.

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